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Cyclic voltammograms from first principles

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Cyclic voltammetry is perhaps the most important and widely utilized technique in the field of analytical electrochemistry. By measuring the current through an electrochemical cell as the cell potential is cycled an abundance of quantitative information regarding surface electrochemical phenomena can be obtained. For over 40 years, general and specific quantitative mathematical relationships have been developed to describe spectra recorded using cyclic voltammetry (1,2). Such expressions are crucial in the interpretation of measured data; however, in and of themselves such expressions offer little predictive ability.

We will here present a straightforward first principles method based on density functional theory calculations for generating theoretical cyclic voltammograms (CVs). The method is applied to a calculation of the CVs for hydrogen under-potential deposition (H-UPD) over Pt(111) and Pt(100) surfaces. The theoretical CVs show excellent agreement with experimental measurements, indicating that we have now a direct link between the energetics of adsorption processes on metal surfaces and experimental CVs.

The method will also be extended to include cyclic voltammograms for water dissociation on Pt(111) and $Pt_3Ni(111)$. The connection between the onset of water dissociation and the activity of the material for the oxygen reduction reaction as given by a previously described theoretical model (3) will be discussed.

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